IFW

FAX RECEIVED

MAY 1 4 2007

OFFICE OF PETITIONS

SANTANGELO Law Offices, P.C.
125 S. Howes, 3rd Floor
Fort Collins, CO 80521
(970) 224-3100   FAX (970) 224-3175
e-mail ideas@IdeaAssetGroup.com

FACSIMILE TRANSMISSION

This message is intended only for the use of the individual or entity to which it is addressed, and may contain information that is privileged, confidential and exempt from disclosure under applicable law. If the reader of this message is not the intended recipient, or the employee or agent responsible for delivering the message to the intended recipient, you are hereby notified that any dissemination, distribution or copying of this communication is strictly prohibited. If you have received this communication in error, please notify us immediately by telephone, and return the original message to us at the above address via the U.S. postal service. Thank you.

TO: Office of Petitions

SPECIAL HANDLING: URGENT DELIVERY REQUESTED

FAX: 571-273-0025   **TELEPHONE:** 571-272-3282

FROM: Al Wiedmann Jr., USPTO Reg. No. 48,033

DATE: May 14, 2007

TOTAL PAGES: *30* (including this cover page) __X__ Facsimile Filing

LETTER OF FACSIMILE TRANSMITTAL

Application Number:	10/789,974
Applicant:	Francis M. Carlson
Filed:	February 28, 2004
Title:	Methods of Evaluating Undersaturated Coalbed Methane Reservoirs
TC/A.U:	3672
Examiner:	Daniel P. Stephenson
Assignee:	Yates Petroleum Corporation
Attorney Docket:	Yates-CDP-US-NProv
Customer No.	33549

Enclosed for immediate filing in the above application please find the following:

1. Petition Under 37 CFR §1.183 (Suspension of Rules);
2. An Information Disclosure Statement, including a list of references cited, and a Statement under 37 CFR §1.97(e)(2), along with copies of non-patent references cited therein;
3. Credit Card Authorization Form authorizing payment of $580.00 ($400.00 for the petition fee under 37 CFR §1.17(f) and $180.00 for the fee under 37 CFR §1.17(p)); and
4. Certificate of Facsimile Transmission.

I have this __14th__ day of May, 2007, either myself personally or through my direction of staff at this

1

office, transmitted all of the items in the above letter of transmittal via facsimile number 571-273-0025, addressed to Office of Petitions.

Dated this 14th day of May, 2007.

FAX RECEIVED

MAY 1 4 2007

Respectfully Submitted,
SANTANGELO LAW OFFICES, P.C.

OFFICE OF PETITIONS

By: _____

Al Wiedmann Jr.
Attorney for Assignee
USPTO Reg No. 48,033
125 South Howes, Third Floor
Fort Collins, CO 80521
(970) 224-3100

Facsimile Number: ~~FAX RECEIVED~~

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

MAY 1 4 2007

OFFICE OF PETITIONS

Application Number:	10/789,974
Applicant:	Francis M. Carlson
Filed:	February 28, 2004
Title:	Methods of Evaluating Undersaturated Coalbed Methane Reservoirs
TC/A.U:	3672
Examiner:	Daniel P. Stephenson
Assignee:	Yates Petroleum Corporation
Attorney Docket:	Yates-CDP-US-NProv
Customer No.	33549

PETITION TO SUSPEND RULES,

UNDER 37 C.F.R. §1.183

Assignee, under 37 C.F.R. §1.183, hereby petitions the US Patent and Trademark Office suspend 37 C.F.R. 1.97(i) as it would otherwise apply in this case at this time. Under ordinary situations, 37 C.F.R. 1.97(i) operates to disallow the consideration of an information disclosure statement filed in non-compliance with 37 C.F.R. 1.97, mandating instead that such information disclosure statement merely "be placed in the file." 37 C.F.R. 1.97(i). In accordance therewith, 37 C.F.R. 1.97(i) operates to disallow the consideration of an Information Disclosure Statement filed after payment of the issue fee, *inter alia*.

Assignee hereby petitions the Office, under 37 C.F.R. §1.183, to suspend 37 C.F.R. 1.97(i) as it would otherwise apply in this case.

As a brief background, the Assignee, on March 1, 2007, paid issue and publication fees in the above captioned application. On April 25, 2007, an Issue Notification was sent from the Patent Office to the Assignee's representative, indicating that the instant application was to issue as a patent on May 15, 2007. On May 8, 2007, Assignee's representative received a letter in which were provided several documents, heretofore unknown to the Assignee or its representatives, which may or may not be material to the examination of the instant application. As such, the Assignee would request that Rule 97(i) be suspended, and the references be considered by the Office before Tuesday, May 15, 2007. If, after such consideration, and as Assignee anticipates, the Office is of the opinion that the claims of the application are indeed patentable over the references enclosed herein, it is requested that the Office allow the patent to issue on May 15, 2007 as originally intended. Such references are cited in the information disclosure statement provided herein, and copies of such references are also provided herein.

The Assignee would submit that, indeed, the circumstances of this case amount to an extraordinary situation, and that justice requires that Rule 97(i) be suspended. More particularly, the Assignee received the attached references precisely one week before the issue date of the patent - a very late point in time in the prosecution. Further, Assignee is of the opinion - and is confident the Office will agree - that the references are either marginally relevant at best, or duplicative of prior art already considered in the application.

Assignee further indicates that it has submitted herewith a statement under 37 CFR §1.97(e)(2), and the fee under 37 CFR §1.17(p).

In summary, Assignee requests that 37 C.F.R. 1.97(i) be suspended so that the information disclosure statement and references cited herewith be considered immediately in this application. Further, if indeed the Office is of the opinion that the claims of the application are indeed patentable over the references enclosed herein, it is requested that the Office allow the patent to issue on May 15, 2007 as originally intended.

Dated this _14_ day of May, 2007.

Respectfully Submitted,
SANTANGELO LAW OFFICES, P.C.

By: _____
Al Wiedmann Jr.
Attorney for Assignee
USPTO Reg No. 48,033
125 South Howes, Third Floor
Fort Collins, CO 80521
(970) 224-3100

2

FAX RECEIVED

MAY **1 4** 2007

OFFICE OF PETITIONS

Facsimile Number: 571-273-0025

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE **LIST OF REFERENCES - INFORMATION DISCLOSURE STATEMENT BY ASSIGNEE**	APPLICATION NO:	10/789,974
	FILING DATE:	February 28, 2004
	FIRST NAMED INVENTOR:	Francis M. Carlson
	ART UNIT:	3672
	EXAMINER NAME:	Daniel P. Stephenson
	DOCKET NO:	Yates-CDP-US-NProv

I.   U.S. PATENT DOCUMENTS

EXAMINER INITIAL	DOCUMENT NO. & KIND CODE (if known)	PUB'N DATE mm-dd-yyyy	PATENTEE OR APPLICANT NAME	Pages, Columns, Lines Where Relevant Passages Or Relevant Drawings Appear

II.   FOREIGN PATENT DOCUMENTS

EXAMINER INITIAL	Foreign Patent Document Country Code, Number, Kind Code (if known)	PUB'N DATE mm-dd-yyyy	PATENTEE OR APPLICANT NAME	TRANSLATION	
				Yes	No

III.   NON-PATENT LITERATURE DOCUMENTS

	Z. Weishauptova and J. Medek, "Bound forms of methane in the porous system of coal," Fuel 1998, Vol. 77, No. 1 / 2, pp 71-76
	J.J. Kipling, "Adsorption from Solutions of Non-Electrolytes," Academic Press 1965, pp 86-89
	I. Gray, "Determining Gas Production Characteristics of Coal Seams," Bowen Basin Symposium 2000, pp 315-320
	Letter dated May 3, 2007 from McCormick, Paulding & Huber LLP to Santangelo Law Offices, PC
	Letter dated May 14, 2007 from Santangelo Law Offices, PC to McCormick, Paulding & Huber LLP

EXAMINER	DATE CONSIDERED

EXAMINER: Please initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.

FAX RECEIVED

MAY 1 4 2007

OFFICE OF PETITIONS

Facsimile Number: 571-273-0025

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application Number:	10/789,974
Applicant:	Francis M. Carlson
Filed:	February 28, 2004
Title:	Methods of Evaluating Undersaturated Coalbed Methane Reservoirs
TC/A.U:	3672
Examiner:	Daniel P. Stephenson
Assignee:	Yates Petroleum Corporation
Attorney Docket:	Yates-CDP-US-NProv
Customer No.	33549

STATEMENT UNDER 37 CFR §1.97(e)(2)

The Assignee respectfully requests consideration of the references in the attached List of References.

It is hereby stated that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing below after making reasonable inquiry, no item of information contained in the information disclosure statement was know to any individual designated in §1.56(c) more than three months prior to the filing of the information disclosure statement.

Thus, as a means of complying with the duty of disclosure set forth in 37 C.F.R. §§1.56, 1.97, and 1.98, the information in the List of References submitted herewith *may* be material to the examination of the referenced application. Pursuant to 37 C.F.R. Section 1.97(g), this Information Disclosure Statement should not be construed as a representation that a search has been made. Additionally, pursuant to 37 C.F.R. §1.97(h) the filing of this Information Disclosure Statement shall not be construed as an admission that the information cited is or is considered to be material to

1

patentability as defined in 37 C.F.R. 1.56(b). A copy of each item listed under Foreign References and Other Documents is enclosed.

Dated this $\underline{14}^{th}$ day of May, 2007.

Respectfully submitted,
SANTANGELO LAW OFFICES, P.C.

By: _____
Al Wiedmann Jr.
Attorney for Assignee
USPTO Reg. No.48,033
125 South Howes, Third Floor
Fort Collins, Colorado 80521
(970) 224-3100

2

FAX RECEIVED

United States Patent & Trademark Office

Credit Card Payment Form
Please Read Instructions before Completing this Form

MAY **1 4** 2007

OFFICE OF PETITIONS

Credit Card Information

Credit Card Type:	[X] Visa	☐ MasterCard	☐ American Express	☐ Discover

Credit Card Account #: ███████████████

Credit Card Expiration Date: 07/31/2010

Name as it Appears on Credit Card: Santangelo Law Offices, P.C.

Payment Amount: $(US Dollars): $580.00   CC447

Signature: _[signature]_   Date: May 11, 2007

Refund Policy: The Office may refund a fee paid by mistake or in excess of that required. A change of purpose after the payment of a fee will not entitle a party to a refund of such fee. The Office will not refund amounts of twenty-five dollars or less unless a refund is specifically requested, and will not notify the payor of such amounts (37 CFR 1.26). Refund of a fee paid by credit card will be via credit to the credit card account.
Service Charge: There is a 50.00 service charge for processing each payment refused (including a check returned "unpaid") or charged back by a financial institution (37 CFR 1.21(m)).

Credit Card Billing Address

Street Address 1: 125 South Howes, 3rd Floor

Street Address 2:

City: Fort Collins

State: CO	Zip/Postal Code : 80521

Country: United States of America

PTO did not receive items marked with *

Daytime Phone #: 970-224-3100	Fax #: 970-224-3175

Request and Payment Information

Description of Request and Payment Information:
Petition and IDS Fees

Patent Fee	Patent Maintenance Fee	Trademark Fee	Other Fee
Application No. 10/789,974	Application No.	Serial No.	IDON Customer No.
Patent No.	Patent No.	Registration No.	
Attorney Docket No. Yates-CDP-US-NPro		Identify or Describe Mark	

If the cardholder includes a credit card number on any form or document other than the Credit Card Payment Form, the United States Patent & Trademark Office will not be liable in the event that the credit card number becomes public knowledge.

Facsimile Number: 571-273-0025

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

FAX RECEIVED

MAY 1 4 2007

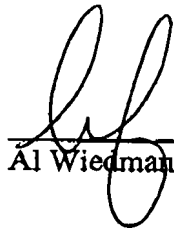**OFFICE OF PETITIONS**

Application Number:	10/789,974
Applicant:	Francis M. Carlson
Filed:	February 28, 2004
Title:	Methods of Evaluating Undersaturated Coalbed Methane Reservoirs
TC/A.U:	3672
Examiner:	Daniel P. Stephenson
Assignee:	Yates Petroleum Corporation
Attorney Docket:	Yates-CDP-US-NProv
Customer No.	33549

CERTIFICATE OF FACSIMILE TRANSMISSION

I, Al Wiedmann Jr., hereby certify to the truth of the following items:

1.   I am an employee of Santangelo Law Offices, P.C., 125 South Howes, Third Floor, Fort Collins, Colorado 80521.

2.   I have this day forwarded the foregoing Petition Under 37 CFR §1.183 (Suspension of Rules); Information Disclosure Statement, including a List of References and a Statement under 37 CFR §1.97(e)(2), along with copies of the non-patent references cited; Credit Card Authorization Form authorizing payment of $580.00 ($400.00 for the petition fee under 37 CFR §1.17(f) and $180.00 for the fee under 37 CFR §1.17(p)); and this Certificate of Facsimile Transmission, via facsimile number 571-273-0025, addressed to Office of Petitions.

Dated this 14th day of May, 2007.

Al Wiedmann Jr.

Bound forms of methane in the porous system of coal

Zuzana Weishauptová[a],* and Jiří Medek[b]

[a]*Institute of Rock Structure and Mechanics, 182 09 Prague, Czech Republic*
[b]*CARBOCHEM, 169 00 Prague, Czech Republic*
(Received 4 November 1996; revised 19 June 1997)

The total quantity of methane present in a coal bed at temperatures above the critical temperature was divided into four basic forms of bonding: the part adsorbed in micropores, the part adsorbed on the meso- and macropores surface, the part freely moving in the pore space which is not filled with water, and finally the part dissolved in the water present in the pores. The sum of the partial volumes mentioned was interpreted as the theoretical isotherm of the total amount of methane occluded in coal; for its evaluation Dubinin's low-pressure isotherm extrapolated to the range of true *in situ* pressures and the volume and surface of meso- and macropores were used. Isotherms computed in this way were in very good agreement with experimental high-pressure isotherms measured up to 10 MPa. For the estimation of methane amount occluded in coal under real mining conditions the theoretical isotherms will be modified by the introduction of correction terms characterizing the changes of the porous system of coal due to water content and overburden pressure. It has been shown that the presence of water content has on the restriction of methane amount a greater effect than the overburden pressure. © *1997 Elsevier Science Ltd.*

(Keywords: coal; gas-bearing capacity; methane)

INTRODUCTION

The methane content in a coal bed can be estimated using two different procedures: (a) directly in the coal mine (*in situ*) by desorption of a defined gas volume from the unworked coal bed and its subsequent analysis; or (b) under laboratory conditions by determination of the gas amount reincorporated into the extracted coal at pressure and temperature comparable with those *in situ*[1–11] (the quoted references are a part of the large set of special contributions, mostly in the form of research reports, concerning technological applications).

The measurement with samples of extracted coal is based on the determination of the quantity of adsorbed methane, which should be, assuming the reversibility of the adsorption/desorption processes, related to the gas amount released by spontaneous or induced degassing. Owing to the fact that the gas in a coal bed is usually present under a pressure, its approximate quantity should be determined by the high-pressure adsorption isotherm within the pressure range of the order of 10^0–10^1 MPa.

According to the high-pressure isotherm, the results mostly approach the coal–gas system in the coal bed. They are interpreted as the sum of methane adsorbed in the pores without distinction of the methane portions contained in the individual parts of the porous system, including the gas dissolved in capillary water.

However, under real conditions in the porous system of coal a freely moving gas is also present[1,2,11], which at higher pore volumes and higher pressures participates significantly in the total amount of bound gas.

The aim of this work was to determine the partial volumes of methane bound by different mechanisms in the individual parts of the porous system of coal and to compare their sum with the results obtained by the high-pressure isotherm.

BOUND FORMS OF METHANE IN COAL

Four partial forms, in which gas in coal is contained, may be assumed. The gas volumes adsorbed (a) in micropores w, (b) in meso- and macropores V_{mma}, (c) the volume of freely moving gas V_{mmg} contained in the free space of meso- and macropores unoccupied with water, and finally (d) the volume of gas dissolved in water V_H.

(a) Sorption of gas in micropores with radii $r < 1.6$ nm is defined by Dubinin's equation[12,13] for volume filling:

$$\Theta_m = \frac{w}{w_0} = \exp\left[D\left(\ln\frac{P}{P_0}\right)^n\right] \tag{1}$$

where Θ_m expresses the degree of the micropores filling, w is the volume adsorbed at the pressure P, w_0 is the volume adsorbed at the complete micropores filling at the saturation pressure P_0, and D and n are constants. At temperatures above the critical temperature the saturation pressure P_0 can be computed as an effective quantity according to Dubinin's approximation:

$$P_0 = P_c \frac{T_s^2}{T_c^2} \tag{2}$$

where P_c and T_c are the critical pressure and temperature, respectively, and T_s is the temperature of sorption.

(b) Sorption of methane in meso- and macropores with

---
* Corresponding author.

Bound forms of methane in coal: ... Weishauptová and J. Medek

radii of $r > 1.6$ nm is realized by deposition of gas molecules into layers. At temperatures above the critical temperature the formation of only a single monolayer may be assumed. Therefore, the maximum number of molecules adsorbed on the surface of meso- and macropores S_{mm} at the saturation pressure P_s will be $N_s = S_{mm}/\sigma$, where σ is the effective contact area of the methane molecule with the solid surface. The volume of methane adsorbed in a monolayer V_{mono} is then given by the relation

$$V_{mono} = \frac{V_M S_{mm}}{\sigma A} \qquad (3)$$

where V_M is the molar volume and A is Avogadro's number. The approximate value of S_{mm} can be determined by mercury porosimetry from the distribution of pores according to their radii and partial volumes.

At the arbitrary pressure $P < P_s$, the number of adsorbed molecules will be $N < N_s$ and the degree of surface coverage $\Theta_{mm} = N < N_s$. In order to simplify the calculation, the estimation can be introduced that the extent of gas adsorption in meso- and macropores is approximately the same as in micropores, so that $\Theta_{mm} = \Theta_m$. Thus the adsorbed volume of methane, at the coverage degree Θ_{mm}, will be

$$V_{mma} = \frac{V_{mono} N}{N_s} = \frac{V_{mono} W}{W_0} \qquad (4)$$

where all necessary quantities can be determined directly.

(c) Freely moving gas is an integral part of methane in the free space of meso- and macropores and its behaviour can be described after introducing a compressibility coefficient z, by the state equation of ideal gas. After conversion into STP, for its volume V_{mmg} at the pressure P (MPa) it holds that

$$V_{mmg} = \frac{273 V_{mm} P}{0.1 z T_a} \qquad (5)$$

(d) The portion of gas dissolved in capillary water obeys Henry's law, so that for its volume V_H at pressure P,

$$V_H = \alpha(T) \cdot W \cdot P \qquad (6)$$

where $\alpha(T)$ is the absorption coefficient and W the water content. The total quantity of methane V_{CH_4} contained in unloaded coal at the pressure P may be obtained as the sum of individual partial volumes according to eqns (1), (4)-(6):

$$V_{CH_4} = (w + V_{mma} + V_{mmg} + V_H) \qquad (7)$$

EXPERIMENTAL

Coal samples

Three samples of bituminous coal from methane-bearing beds of the Ostrava area were used. Their basic chemical and textural characteristics are listed in *Table 1*. All measurements were performed using water-free samples.

Experimental methods

The volume of meso- and macropores V_{mm}, their surface area S_{mm} and apparent density d_a were determined with particles of 2–3 mm in size using a high-pressure mercury porosimeter Micromeritics pore sizer 9310.

The determination of the low-pressure isotherms of methane was performed at a temperature T_a of 298K within the pressure range from 0.01 to 0.15 MPa with a Sorptomatic 1800 apparatus. According to eqn (2), for methane the value $P_0 = 11.2$ MPa for $P_c = 4.58$ MPa and $T_c = 190.7$K was obtained. For exponent n, the value of 2 was found to be an optimum one.

The high-pressure isotherms were determined at 298K by the volume method with an apparatus schematically illustrated in *Figure 1*. For pressure measurement within the range 0.1–10 MPa a digital electronic transducer with a precision reading of ± 0.001 MPa was used. The pressure interval has been chosen with regard to the conditions *in situ*. The volumes of the separate sections of the apparatus were determined by direct engineering measurements and the assembled experimental unit was calibrated with methane within the pressure range mentioned. The deviations from the behaviour of an ideal gas were corrected by empirical coefficients. In order to include into pressure and volume changes also the actual state of freely moving gas in pores, the value of the apparent volume d_a of coal has been introduced for the correction of the gas volume in cell 1. The sorption equilibrium attained after several hours was indicated by minimum changes of recorded pressure within the range of ± 0.002 MPa.

At the beginning of the measurement of both low- and high-pressure isotherms the coal samples with the grain size below 0.2 mm were evacuated at 350K to 10^{-2} Pa for 5 h. For high-pressure measurement their weight varied between 30 and 50 g.

For computing of the quantities V_{mono} and V_H the following values were introduced into eqn (3) and eqn (5): $V_M = 22\,414$ cm^3 mol^{-1}, $\sigma = 16.10^{-14}$ cm^2, $\alpha(298) = 0.331$ cm^3 cm^{-3}P. Since the water density is very close to 1.0 g cm^{-3}, the water volume in pores may be expressed as $0.01W$, where W is the water content (wt%).

RESULTS

Figures 2–4 show the experimental high-pressure isotherms together with the theoretical ones, which represent the sum of partial volumes w, V_{mma} and V_{mmg}. Their dependence on pressure is illustrated by separate isotherms. Volumes w relating to higher pressures up to the saturation pressure P_0 were calculated by extrapolation of eqn (1), similarly volumes V_{mma} and V_{mmg} according to eqns (4) and (5), respectively. For the comparison of experimental and theoretical isotherms, the corrections for the overburden pressure and water content were not introduced.

Figures 5–7 interpret experimental and theoretical

Table 1 Basic chemical and textural characteristics of coal

Sample	W	Ash (wt%)	V^{daf}	V_{micro} (cm^3 g^{-1})	V_{mm} (cm^3 g^{-1})	S_{mm} (m^2 g^{-1})
A	0.8	2.2	29.2	0.122	0.087	7.62
B	0.7	8.9	29.1	0.063	0.033	7.03
C	1.4	2.5	33.6	0.044	0.049	8.00

W = water content, V^{daf} = volatile matter (dry and ash free basis), V_{micro} = volume of micropores, V_{mm} = volume of meso- and macropores, S_{mm} = surface area of meso- and macropores.

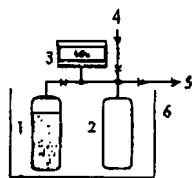*Bound forms of methane in coal: Z. Weishauptová and J. Medek*

Figure 1 Schematic diagram of high-pressure sorption apparatus. (1) Sample cell; (2) reference cell; (3) electronic digital pressure transducer; (4) methane pressure bottle; (5) vacuum pump; (6) constant temperature air bath
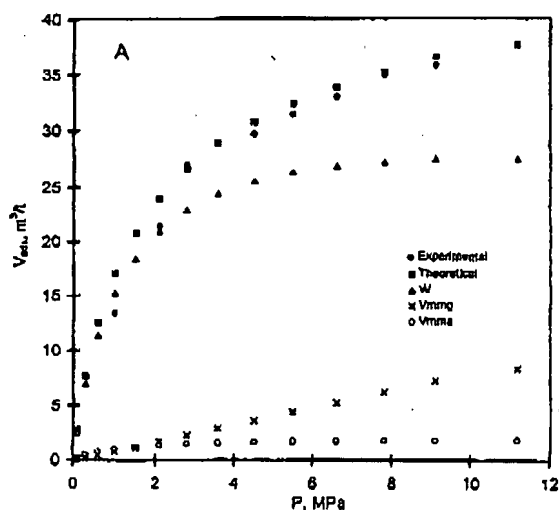

Figure 2 Theoretical and experimental high-pressure isotherms of methane on coal A. The theoretical isotherm is the sum of partial volumes w, V_{mma} and V_{mmg}
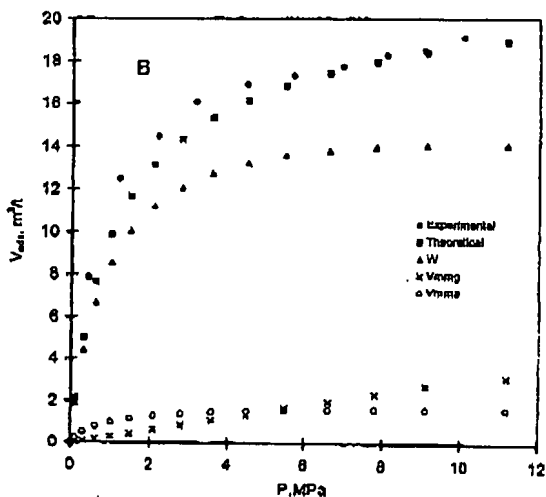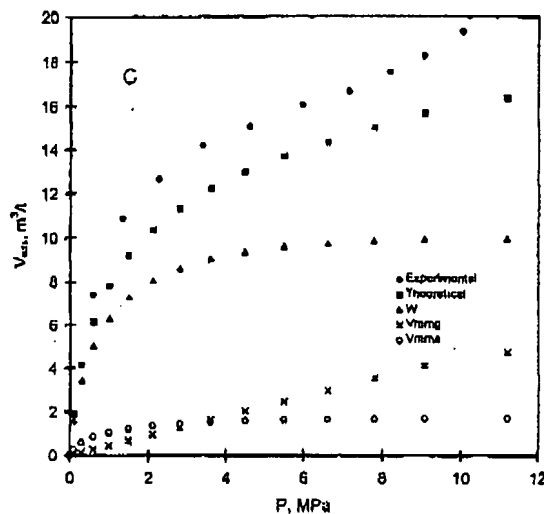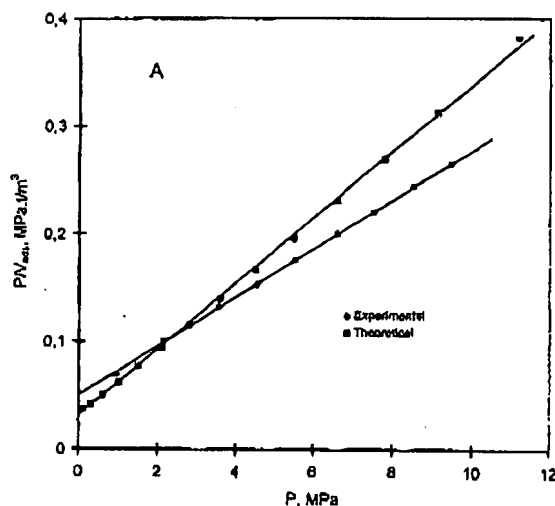

Figure 3 Theoretical and experimental high-pressure isotherms of methane on coal B. The theoretical isotherm is the sum of partial volumes w, V_{mma} and V_{mmg}

Figure 4 Theoretical and experimental high-pressure isotherms of methane on coal C. The theoretical isotherm is the sum of partial volumes w, V_{mma} and V_{mmg}

Figure 5 Theoretical and experimental high-pressure isotherms on coal A in Langmuir's coordinates. The experimental isotherm fulfils the linearity with correlation coefficient $r_{exp} = 0.9982$ and the theoretical one with $r_t = 0.9999$

isotherms, the last one involving only the sum of adsorbed volumes w and V_{mma}, in the coordinates of the linear form of Langmuir's equation[14].

DISCUSSION

Comparison of low- and high-pressure isotherms

From *Figures 2 and 3* for samples A and B, respectively, it is evident that there is a practically complete agreement of experimental and theoretical isotherms, their shape being very similar to each other as well. For the sample C (*Figure 4*), the theoretical isotherm lies somewhat lower;

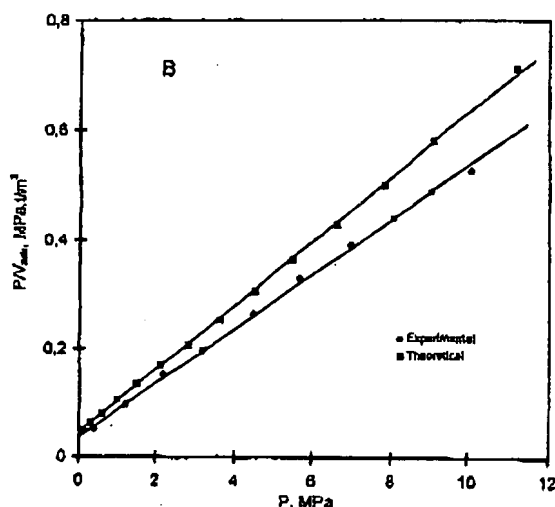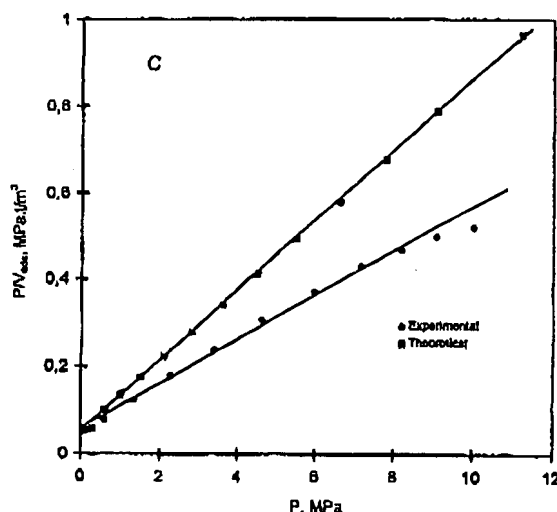*Bound forms of methane in coal: L. Weishauptová and J. Medek*

Figure 6 Theoretical and experimental high-pressure isotherms on coal B in Langmuir's coordinates. The experimental isotherm fulfils the linearity with correlation coefficient $r_{exp} = 0.9993$ and the theoretical one with $r_t = 0.9998$

Figure 7 Theoretical and experimental high-pressure isotherms on coal C in Langmuir's coordinates. The experimental isotherm fulfils the linearity with correlation coefficient $r_{exp} = 0.9849$ (within a pressure interval from 0.5 to 8.5 MPa) and the theoretical one with $r_t = 0.9993$

however, the difference between the V_{ads} values of both isotherms is 10% on average, which can also be considered a fair correspondence in this case. The shape of both isotherms is coincident up to the pressure of 8 MPa; with the increasing pressure, the experimental isotherm curves towards higher values. This deviation, as well as higher V_{ads} values within the entire pressure range, can be explained with sample C by distinct methane absorption by the coal matrix, which increases at higher pressures[15].

Distribution of methane in the porous system

From the present results it follows that the dominant part of methane is bound in micropores. This fact is in agreement with present opinions concerning the textural character of coal[16] and with the conception that the fundamental form of the coal matter[17] is the microporous phase.

The approximately full saturation of the micropores with methane takes place in about the middle of the pressure range from $P = 0$ to P_0 and the further course of the isotherm is nearly parallel to the pressure axis. In contrast, the high-pressure isotherms run practically from the beginning above the theoretical one, rising continuously. This difference between the volume V_{ads} according to the high-pressure isotherm and the volume w according to Dubinin's isotherm corresponds to the contribution of two other considered forms of gas bonding in the porous system of coal. According to *Figures 2–4*, the smaller part relates to gas adsorbed on the surface of meso- and macropores and the larger part to the free gas contained in the pores. Owing to the temperature above the critical temperature, the maximum adsorbed quantity of methane V_{mma} should be attained in a finished monolayer, while the quantity of free gas V_{mmg}, at the constant volume of meso- and macropores, increases with pressure without limits according to the equation of state [eqn (5)].

The adsorption of methane on coal at temperatures above the critical temperature within the range of very low relative pressures, when the part of adsorbed gas in meso- and macropores is negligible, easily satisfies Dubinin's equation of volume filling of micropores. At pressures of the order of tens of MPa, the adsorption is currently interpreted by Langmuir's equation in linear form:

$$\frac{P}{V_{ads}} = \frac{1}{V_L P_L} + \frac{P}{V_L} \tag{8}$$

where V_L is the gas volume adsorbed in monolayer as the pressure approaches infinity and P_L is the pressure at which the volume $V_{ads} = V_m/2$. These two Langmuir's constants are useful for the interpretation of degasification conditions. From *Figures 5–7* it is evident that eqn (8) in its linear form corresponds better to the theoretical isotherms, which reflect only the adsorbed volumes w and V_{mma}. In *Table 2* both constants V_L and P_L evaluated from the course of linearized isotherms are presented. The differences of V_L and P_L between theoretical and experimental isotherms are caused by the different methane amount included in the quantity V_{ads}. The volume V_{ads} of the experimental high-pressure isotherm contains all partial gas volumes including the freely moving gas, which cannot be distinguished, whereas V_{ads} of the theoretical isotherm presents only the sum of adsorbed volumes. Therefore the values of V_L will be, in the first case, always higher. A more detailed interpretation of Langmuir's parameters for practical purpose is the subject of a future paper.

Application of theoretical isotherms to the estimation of potencial methane content in the coal bed

For the estimation of methane amount occluded in coal under practical mining conditions *in situ* the theoretical isotherms measured with dry samples of extracted coal will be modified by the introduction of correction terms characterizing the changes in the porous system of coal due to water content and overburden pressure.

When the coal is loaded by overburden pressure sg (MPa) and the water content is W (wt%), after complete correction

Table 2 Parameters of Langmuir's equation of experimental and theoretical isotherms

Sample	Isotherm Experimental V_L (m³ t⁻¹)	P_L (MPa)	Theoretical V_L (m³ t⁻¹)	P_L (MPa)
A	44.02	2.20	32.88	1.15
B	20.17	0.77	16.70	0.78
c	16.40	0.69	12.37	0.62

V_L = volume of gas adsorbed in monolayer, P_L = pressure corresponding to $V_{aH} = V_L/2$.

(the compressibility of water in pores is negligible) the free volume of meso- and macropores V_{mm} of unloaded coal will be reduced to

$$V^*_{mm} = V_{mm}e^{-\beta sg} - 0.01W \tag{10}$$

where β is the coefficient of coal compressibility, whose average value[2] can be estimated to 0.002 MPa⁻¹. If $0.01W \geq V_{mm}e^{-\beta sg}$, then $V^*_{mm} = 0$. Substituting V^*_{mm} for V_{mm} in eqn (5) the volume V^*_{mmg} of freely moving gas in restricted pore space will be obtained.

With respect to the very small consequence of methane volume adsorbed on meso- and macropores surface S_{mm}, a simple relation between V_{mm} and S_{mm} in the form $S_{mm} = 2V_{mm}/\bar{r}$ may be used, where $\bar{r}$ is the mean radius of cylindrical meso- and macropores, or in the case of slit-shape pores, $S_{mm} = 2V_{mm}/\bar{r}$, where $\bar{r}$ is the half-width distance between two parallel plates. Assuming that the occupation of these pores with water is uniformly distributed within the whole meso- and macropores system, the quantity of $\bar{r}$ remains nearly constant and the changes in S_{mm} are directly proportional to those in V_{mm}. Therefore, the free part S^*_{mm} unoccupied by water molecules, can be assumed to equal

$$S^*_{mm} = \frac{S_{mm}V^*_{mm}}{V_{mm}} \tag{11}$$

For the volume of methane adsorbed at pressure P on the nonwetted surface S^*_{mm}, after numerical evaluation of the constants in eqn (3), it holds that

$$V^*_{mma} = \frac{0.233S_{mm}V^*_{mm}w}{V_{mm}W_0} \tag{12}$$

However, in a moist coal a part of the surface S^*_{mm} is always occupied by adsorbed water molecules. For the correction for partial coverage of S^*_{mm} simple Ettinger's relation[18] has been used:

$$\frac{V^W_{mma}}{V_{mm}} - = \frac{1}{(kW + 1)} \tag{13}$$

where V_{mma} means the adsorbed volume of methane on the surface of water-free coal and V^W_{mma} the same of coal with a water content W (wt%). After neglecting the correction for 'critical' water content[3,4] which requires the determination of oxygen content, the average value of 0.3 has been attributed to the constant k. Then, after combining eqns (12) and (13), for the amount of methane adsorbed at the pressure P on the surface S^*_{mm} partially coverd with water molecules it holds that

$$V^{*W} = \frac{0.233S^*_{mm}V_{mm}w}{V_{mm}[(kW + 1)]w_0} \tag{14}$$

After replacement of V_{mma} by V^{W*}_{mma} and of V_{mmg} by V^*_{mmg} in eqn (7) and assuming that the methane abundance equals
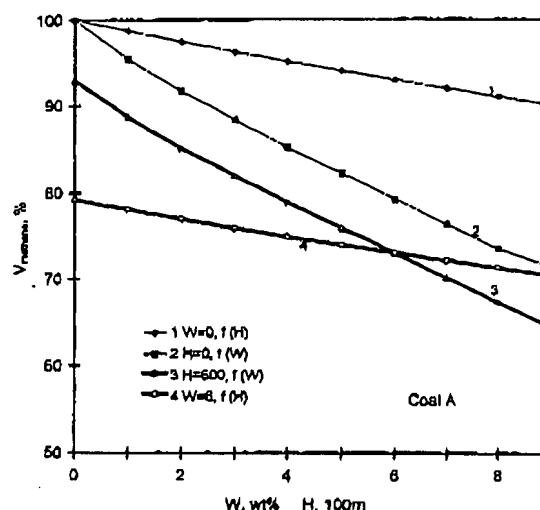

Figure 8 Reduction of methane content in coal A as function of water content W and bed depth H. Theoretical isotherms were computed according to eqn (13) for $T = 298$K

100%, the following may be written:

$$V_{CH_4} = \left(w + V^{*W}_{mma} + V^*_{mmg} + V_H\right) \tag{15}$$

Influence of water content and overburden pressure on methane content in the coal bed

According to eqn (15) the theoretical isotherms for coal A were calculated. The reduction of the gas volume in pores with different water contents and at different overburden pressures are shown in *Figure 8*. The scale at the abscissa gives directly the values of water content W (wt%) and, multiplied by scale factor of 100, the depth of bed H (m). According to the value of V_{mm} in *Table 1*, at $W = 8.7$ wt% the porous system of coal is filled completely. The ordinate gives the relative methane content $V_{methane}$ (%) in coal, where the value of 100% pertains to complete saturation of dry and unloaded coal. The fine line 1 shows the decrease in $V_{methane}$ in dry coal in dependence on overburden pressure sg. Its quantity was expressed by the bed depth, assuming that the average rock density is 2.3 t m⁻³. The fine line 2 shows the decrease in $V_{methane}$ in unloaded coal as a function of water content. The heavy lines illustrate the changes including the effect of both overburden pressure and water content. The heavey line 3 represents the decrease in $V_{methane}$ in coal containing $W = 6$ wt% as a function of depth, and the heavy line 4 shows its changes with water content in coal at the bed depth of 600 m.

The effect of moisture on the quantity of methane in coal may differ accordingly, as water may already be present in the bed coal or is presorbed onto the pre-dried coal.

Bound forms of methane in coal: _. Weishauptová and J. Medek

Assuming that the filling of micropores with methane during the genesis of coal was a primary event[2] and that it did not change with water coming into contact with coal, only the gas amount present in meso- and macropores depends on the water content. However, its changes cannot be decisive for the gas-bearing capacity. In the case of evacuated dry coal, the contact with water vapour causes a partial filling of micropores, whose extent depends on vapour pressure and time of contact. In this way the sorption of methane may be reduced substantially.

The quantity V_H of methane dissolved in liquid water contained in the meso- and macropores has only a limited significance for the total volume of gas and for prediction of the gas content in coal bed it may be neglected. In coal A, for example in the case of maximum filling of the meso- and macropores with water (8.7 vol%), the participation of volume V_H in the total volume is only 0.08% and its quantity—unlike that of carbon dioxide—cannot affect the total amount of combined gas, not even at high partial pressures. More noticeable is the effect of water content on the reduction of volumes V_{mma} and V_{mmg} caused by the blocking of a part of the volume and surface of pores.

CONCLUSIONS

The total amount of methane contained in the porous system of coal may be divided into the part adsorbed in both micropores and meso- and macropores, the part in the form of freely moving gas in the unfilled space of pores, and the part dissolved in the present water. The sum of these partial volumes, determined separately, equals the total volume of methane in coal, the latter corresponding practically to the volume measured by high-pressure adsorption. The division of the total gas volume into individual portions provides the possibility of introducing correction parameters for changes of the size of the porous system due to the water content and the overburden pressure.

ACKNOWLEDGEMENTS

REFERENCES

1   Moffat, D. H. and Weale, K. E., *Fuel*, 1955, 34, 449.
2   Skotchinskij, A. A. and Chodot, V. V., *Metan v Ugolnych Plastach*. Ugletechizdat, Moscow, 1958.
3   Kayser, H. G. and Peters, U., in *Papers of 7th International Conference on Coal Science*, Prague, 1968, 1/62.
4   Joubert, J. L. Grein, C. T. and Bienstock, B., *Fuel*, 1973, 52, 181.
5   Joubert, J.I., Grein, C. T. and Bienstock, B., *Fuel*, 1974, 53, 186.
6   Kissell, F. N., McCulloch. C. M. and Elder, C. H., US Bureau of Mines, R.I. no. 7767, 1973.
7   Kim, A. G., US Bureau of Mines, R.I. no. 8245, 1977.
8   Bell, G. J. and Rakop, K. C., *61st Annual Technical Conference and Exhibition of Society of Petroleum Engineers*, New Orleans, LA, 1986, Paper SPE 15454.
9   Jones, A. H., Bell, G. J. and Schraufnagel, R. A., in *Rocky Mountain Association of Geologists*, ed. J. E. Fasset, Denver, CO, 1988, p. 169.
10 Mavor, M. J., Owen, L. B. and Pratt, T. J., *65th Annual Technical Conference and Exhibition of Society of Petroleum Engineers*, New Orleans, LA, 1990, SPE Paper 20728, p. 157.
11 Lu, X. C., Li, F. C. and Watson, A. T., *Fuel*, 1995, 74, 599.
12 Dubinin, M. M., *Industrial Carbon and Graphite*. Society of Chemical Industry, London, 1958, p. 219.
13 Dubinin, M. M., *Journal of Colloid and Interface Science*, 1967, 23, 487.
14 Langmuir, I., *Journal of the American Chemistry Society*, 1918, 40, 1361.
15 Ceglarska-Stefahska, G., *8th International Conference on Coal Science*, CSIC, Oviedo, 1995, Extended Abstract, Vol. I, p. 27.
16 Vahrman, M., *Fuel*, 1970, 49, 5.
17 Medek, J. and Weishauptová, Z., *Uhli (Coal)*, 1987, 35, 170.
18 Ettinger, I.L. and Lidin, G.D., *Izv. Akad. Nauk SSSR, Otd. Tekh. Nauk*, 1950, 8, 1198.

Adsorption from Solutions of Non-Electrolytes

J. J. KIPLING

Department of Chemistry
The University of Hull
England

1965

ACADEMIC PRESS
LONDON · NEW YORK

PREFACE

Adsorption from solutions of non-electrolytes is given little or no attention in current textbooks of physical chemistry. This may seem surprising in view of the many empirical uses which have been made of the phenomenon in chemical technology over many decades, notably in the purification of liquids, the separation of solutes, and the stabilization of dispersions (e.g. paints, printing ink).

The state of the literature suggests a probable explanation. As can be seen from the two volumes of Deitz's extremely useful *Bibliography of Solid Adsorbents*, the large number of research papers on the solid-liquid interface consists of isolated groups of two or three. Many authors have carried out one investigation of adsorption from solution and have then turned their attention elsewhere. Very few have spent enough time in the field to be able to reflect on its development and so produce a synoptic account of the subject. Without such general reviews or even lectures, the writers of textbooks have had no firm starting-point. Nor could they, as has been possible with other branches of physical chemistry, associate the early investigations with one of the great names of the classical period; adsorption from solution has had no Faraday, Arrhenius, or van der Waals. (It is worth pondering the question why we are now learning more from the mathematician Gibbs than from the experimentalist Freundlich.)

I have argued elsewhere that the early experiments did not provide the best foundation for building a theory of adsorption. Naturally enough, dilute aqueous solutions were used. This focused attention on the solute, and the solvent was ignored—a cardinal error when more concentrated solutions eventually came to be studied. Moreover, water (all too popular as a solvent) is not only quite untypical of solvents generally, but also gives more complex solutions than almost any other solvent.

The advent of World War I increased interest in the adsorption of gases by solids, and many chemists, concerned only incidentally with adsorption from solution, overlooked the difference between adsorption of a one-component gas and a two- (or multi-) component liquid. Slavish use of the Freundlich and Langmuir equations for adsorption isotherms has almost certainly done more harm than good to the theory of adsorption from solution.

In the last few years, however, more consistent attention has been given to the subject in a number of laboratories, which are trying to co-ordinate their results in spite of difficulties arising from distance, language, and international politics. Enough has now been done to show the probable scope of the subject. I have therefore judged it timely to attempt to sketch an outline map. Some of the detail has also been filled in; much, of course,
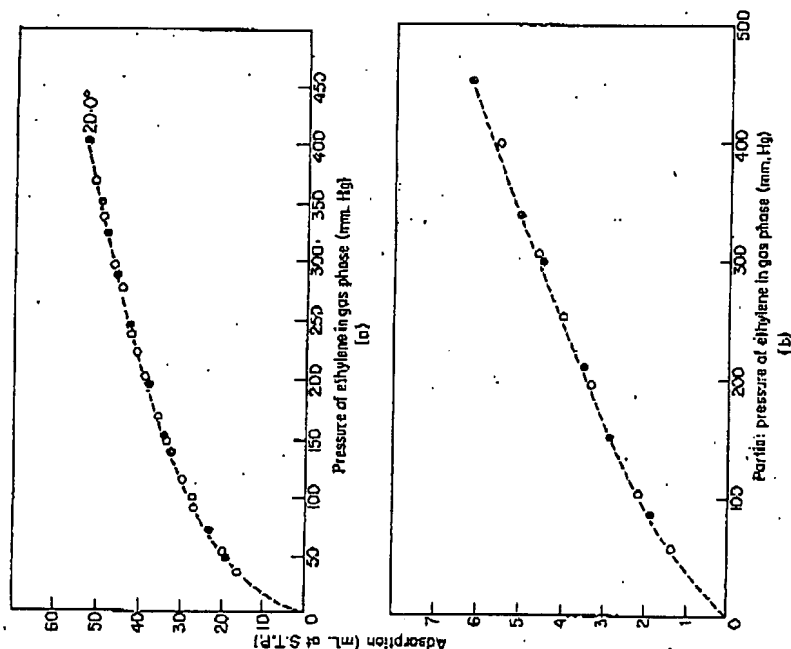
6. ADSORPTION OF GASES FROM SOLUTION

Fig. 6.1. Adsorption of ethylene on charcoal[1] (a) from the gas phase, (b) from aqueous solution, at 20°c. (Reproduced with permission from Acta Chimica Acad. Sci. Hung.).

The latter reacts with the charcoal to form a surface complex which may slowly decompose to give carbon monoxide and carbon dioxide. The break-down is likely to be incomplete, and the retention of some oxygen lowers the efficiency of the charcoal in further dechlorination. The nature of the transient complexes is not clear. The existence of the permanent complexes, however, is demonstrated by heating the charcoal to 400°C, when the two oxides of carbon are evolved in large quantities and the efficiency of the charcoal in dechlorination is restored.

Using static (i.e. batch) conditions, Puri confirmed the formation of hydrochloric acid, but was unable to detect the evolution of oxides of carbon during the adsorption process.[3] He did, however, confirm the chemisorption of oxygen by the charcoal, the quantity recoverable being almost equivalent to the hydrochloric acid formed in the early stages of the process. In the

CHAPTER 6

Adsorption of Gases from Solution

NON-REACTING SYSTEMS

Little attention has been paid to this aspect of adsorption except in respect of gases which ionize in water (e.g. hydrogen chloride) and which behave, as electrolytes. These are not considered here.

The adsorption of ethylene by charcoal at a given pressure is very much less if the charcoal is suspended in water than if it is dry. This is because, in the former case, the ethylene can only come into contact with the charcoal through the medium of its saturated solution in water. From the Bunsen coefficient, the concentration in solution can be calculated as a function of pressure in the gas phase. Alternatively, a "gas-pressure" corresponding to the concentration of the solution can be calculated. The adsorption isotherm, plotted against this equivalent "gas-pressure", can be fitted by a Freundlich equation. The pre-exponential factor is about one-tenth of that for adsorption directly from the gas phase, whereas the exponential factor is about 1·5 times as large as that for direct adsorption, cf. Fig. 6.1. This shows that there is competition between the ethylene and water for the solid surface when adsorption takes place from solution.[1]

In general, it may be expected that adsorption of most gases from solution will follow this pattern. The extent of adsorption is likely to be very small unless the gas reacts with the solid surface. Consequently systems of this kind are neither easy to investigate experimentally, nor of much practical interest.

ADSORPTION WITH REACTION

Adsorption from Chlorine Water

A more complex process occurs in the adsorption of chlorine from aqueous solution by water. This is essentially different from the previous system because chemical reaction takes place between the solute and solvent. The possibility therefore exists of extensive adsorption appearing to take place, but the adsorbed species being actually a reaction product.

The phenomenon is of technological interest in the dechlorination of water supplies and has been reviewed by Magee.[2] It is usually carried out as a column process. The most important step now appears to be adsorption of hypochlorous acid. This subsequently decomposes, on the surface, to give hydrochloric acid and nascent oxygen. The former is released into solution.

85

6. ADSORPTION OF GASES FROM SOLUTION   89

carbons have practically no surface complexes, there are no centres for chemisorption, and it is probable that only physical adsorption takes place. In this process, the important feature is the volatility of both chlorine and the solvent, as each presents chlorine atoms to the surface of the absorbent.

Extensive adsorption occurs on Spheron 6 (1000°C), which retains some hydrogen on the surface, and on unheated Spheron 6, the surface of which is probably covered with oxygen and hydrogen complexes. The majority of the chlorine is probably chemisorbed, but as the isotherm for Spheron 6 shows dependence on concentration, some physical adsorption may also occur. Chemisorption in this case could involve addition of chlorine to double bonds or displacement of hydrogen with simultaneous formation of hydrogen chloride. If the latter process occurred, the points in Fig. 6.2 would represent total removal of chlorine from solution, and only a part of this amount would be adsorbed, the remainder being returned to solution as hydrogen chloride.

REFERENCES

1. T. Erdey-Grúz and F. Nagy, Acta Chim. Acad. Sci. Hung., 1957, 12, 101.
2. V. Magee, Ph.D. Thesis, University of London, 1955.
3. B. R. Puri, D. D. Singh, J. Chander, and L. R. Sharma, J. Indian Chem. Soc., 1958, 35, 181.
4. B. R. Puri, O. P. Mahajan, and D. D. Singh, J. Indian Chem. Soc., 1960, 37, 171.
5. B. R. Puri, "Proceedings of the Fifth Conference on Carbon", Pergamon Press, Oxford, 1962, p. 165.
6. P. V. Shooter, unpublished results.

88   ADSORPTION FROM SOLUTIONS OF NON-ELECTROLYTES

later stages, the amount of oxygen chemisorbed reached a constant value, but hydrochloric acid was still formed, together with a corresponding quantity of chloric acid.[4] It thus appears that the reaction

$$3Cl_2 + 3H_2O \rightarrow 5HCl + HClO_3$$
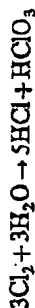
occurs in the later stages, the charcoal acting as a catalyst. The observation of this latter reaction may depend on the use of solutions more concentrated (2660 p.p.m.) than those used in Magee's experiments (10–100 p.p.m.). No evidence was found for the chemisorption of chlorine by charcoal.[5] In this respect chlorine in aqueous solution differs from bromine in aqueous solution (see Chapter 5) and in non-aqueous solutions (see below).
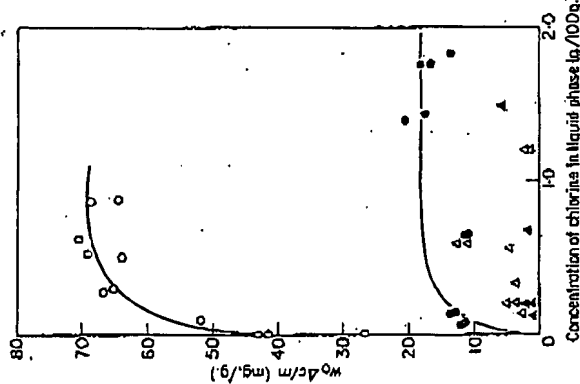

Fig. 6.2. Adsorption by carbon blacks from solutions of chlorine in carbon tetrachloride at 20°c: O, Spheron 6; ●, Spheron 6 (1000°c); △, Spheron 6 (1400°c); ▲, Graphon.[6]

Adsorption of Chlorine from Non-aqueous Solutions

The adsorption of chlorine from non-aqueous solutions should be simpler. There are few simple organic solvents, however, with which chlorine does not react at an appreciable rate at room temperature. The most useful for investigating adsorption is carbon tetrachloride.

The adsorption of chlorine from carbon tetrachloride on a series of related carbon blacks is shown[6] in Fig. 6.2. On Graphon and Spheron 6 (1400°C),† adsorption is too small to be measured accurately. As these

† Spheron 6 (1400°c) refers to the carbon formed by heating Spheron 6 to 1400°c in an inert atmosphere.

IAN GRAY

DETERMINING GAS PRODUCTION CHARACTERISTICS OF COAL SEAMS

Unwinding the mysteries of a coal seam methane reservoir can be substantially achieved without recourse to expensive production trials. This paper examines the options for obtaining the production characteristics of coal seams more efficiently in terms of cost and time, than production tests. The techniques reviewed include DST testing from within HQ wireline core rods, sorption pressure testing, measurement of diffusion coefficients and core permeability testing.

The information gained from the suite of tests includes diffusion coefficient, coal block size, matrix permeability, fracture permeability, reservoir pressure, sorption pressure, gas content and the effects of shrinkage on permeability.

THE CHARACTERISTICS OF COAL SEAM RESERVOIRS

Coal Seams are very complex gas reservoirs. The gas they store is held unconventionally and they may show several levels of permeability. Sometimes permeability increases with extraction whilst in other cases it decreases. Some reservoirs may be treated as homogeneous and modelled using derivatives of conventional reservoir models. Others however behave as a series of domains of different characteristics separated by preferential flow paths. They may be recharged or drained via these flow paths. A knowledge of the reservoir characteristics is invaluable prior to starting gas production, or planning to de-gas a mine.

Gas Storage

The gas contained in coal seams is mostly stored in the coal itself by a process called sorption. Much less gas is stored in pore space either as free gas or in solution in seam water. The reservoirs may be either saturated with water or contain free gas prior to extraction. The gas is stored in the coal at sorption pressure which is the equivalent of the bubble point in a conventional reservoir. The sorption pressure may be less than the reservoir pressure or in the case of a reservoir with free gas, at reservoir fluid pressure.

The gas storage characteristics are commonly represented by the volume stored (at STP) versus pressure relationship for a given temperature. Such relationships are often described by the langmuir isotherm which fits most but notably not all experimental sorption data.

The sorption isotherm is affected by gas type, and the history of how the gas came to be present in the coal. Cases have been noted in high rank coals where CO_2 has been introduced of the CO_2 being released first despite its apparently greater affinity for the coal. It is suspected that this is due to the CH_4 being sited preferentially closer to the surface sites in the coal than the CO_2 which is usually added during a cycle of igneous intrusion. Thus the history of CO_2 then CH_4 generation and CO_2 intrusion (probably as hydrothermal events) becomes important from a time perspective in determining the nature of the sorption isotherm and the gas type released.

The sorption isotherms measured in the laboratory are known to be affected by their moisture content (saturation). This is almost certainly related to the coal being either gas wet or water wet and is associated with competition for sites at molecular level.

The consequence of this is that simple laboratory isotherm testing is not adequate to determine the gas storage characteristics in a seam.

Thus measuring a gas content by core desorption and then re-testing the ground and dried core for a sorption isotherm and using the combined information to arrive at a sorption pressure may be significantly in error. This error is not solely due to the problems in measuring the sorption isotherm but is also brought about by the uncertainties in the measurement of gas content. Specifically the estimation of the gas lost whilst pulling the core remains an issue. Together these uncertainties may lead to significant errors in estimates of sorption pressures especially in the areas of higher gas content where the sorption isotherm shows a high rate of change of pressure for a given change in stored volume.

In essence the requirement is therefore to measure the original gas content and pressure at a few points and thus derive a native sorption isotherm.

Gas Movement

Diffusion

Gas movement appears to occur from within the coal to the cleat structure by a process of diffusion. The speed of the diffusion is dependent on the diffusion coefficient, the cleat spacing and the concentration gradient.

Bowen Basin Symposium 2000

316   Seam Gas

It is relatively straightforward to determine the diffusion coefficients by examining the rates of gas release from core and by assuming the core is a uniform cylinder.

Typically the core displays two diffusion coefficients, an initial one and then a long term one. Typically the short term diffusion coefficient is an order of magnitude greater than the long term coefficient. Occasionally a third diffusion coefficient appears to exist during the long term diffusion process.

The change between short and long term diffusion coefficient is quite marked. It is not yet known whether this change is brought about by pressure changes and as such is essentially a pressure sensitive effect on a quasi-darcy flow or is truly a separate gas release process. The assumption that the coal core is a cylinder must be considered inaccurate in the case of cleated coal.

For these reasons the determination of diffusion coefficients are the subject of ongoing research.

As the rate of diffusion is strongly related to the size and shape of the coal blocks *in situ* from which the gas is escaping the determination of these dimensions is important.

Matrix Permeability

Matrix permeability exists in the cleats where two phase (gas and water) darcy flow takes place down a potential (principally pressure) gradient. During the drainage cycle the permeability changes due to changes in water saturation and due to effective stress variations in the coal. Effective stress is the difference between the total stress, which varies with direction, and the fluid pressure.

Permeability reduces with effective stress in coals. The softer and more cleated the coal, the more dramatic this reduction is. Thus as a coal seam gives up fluid the effective stress might be expected to increase due to reduced pore pressure. This is often not the case.

The reason for this is that the effective stress is not solely related to the fluid pressure but also to the gas content of the coal. It has been shown repeatedly that the change in linear dimension of a piece of coal is dependent on changes in gas content. With reference to seam drainage this dimensional change is one of shrinkage.

Most coal seams are bounded by significantly stiffer roof and floor rocks and therefore the the lateral dimension of the seam is more or less constant but the vertical dimension is free to move. In this environment the total vertical stress in the seam can be expected to remain constant but the effective vertical stress will increase with fluid removal.

In the absence of shrinkage lateral effective stress could be expected to increase due to a reduction in seam fluid pressure. The lateral effective stress increase would be less than the vertical stress increase because the seams are laterally extensive and usually bounded by much stiffer roof and floor rocks. Shrinkage tends however to reduce the coal dimension and with it the effective stress.

The two effects on effective stress are opposing and without adequate testing it is not possible to determine whether matrix permeability will increase or decrease. From field experience both cases are known to exist. The matrix permeability can in some reservoirs change by orders of magnitude with gas production. This change may increase or decrease permeability. Knowing which is vital. Because cleats are directional and stress is directional the matrix permeability is also directional, though fracture permeability may mask this feature in many instances.

Fracture Permeability

Frequently major joint sets also exist within the coal seam and lead to a second level of greater permeability. Major faults may also transect the coal seam acting as barriers, fluid sources or sinks.

Domains

Some coal seam reservoirs behave as though they contain quite different domains with significantly differing properties. These domains are known in some instances to be bounded by faults and are thus structurally different.

AN APPROACH TO RESERVOIR ASSESSMENT

The author's company has developed a procedure for determining coal seam reservoir behaviour. This in essence involves the following process.

Initially a general geological appraisal of an area is made to determine the factors that may influence gas storage or movement. Once the basic geology is understood the programme focuses on drilling and downhole testing.

Use is made of slimhole drilling with wireline coring (usually using the Longyear HQ-3 system) through the coal bearing strata. Slim holes are cheap to drill and wireline core retrieval provides core quickly for gas content measurement, the assessment of diffusion coefficient, shrinkage and permeability testing. Coal thickness can be readily determined and a hole is available for stress and *in situ* permeability testing.

Stress Measurement

Stress measurements are made in the non-coal strata utilizing overcoring or hydrofracture. Measurements are usually made in rock because reliable stress measurement is difficult to achieve in coal by either method. The results are then interpreted in terms of tectonic strain through the sequence so that the coal stress may be estimated on the basis of its modulus and Poisson's ratio.

Bowen Basin Symposium 2000

Core Desorption

Core is withdrawn from the core barrel by wireline and placed in a canister for initial desorption. The initial desorption process is required so that an estimate may be made of the lost gas on core retrieval. The initial period of desorption (~30 minutes) also provides information on the initial diffusion coefficient.

The core should then be transferred to a water-filled pressure vessel and sealed and allowed to come to equilibrium pressure. Desorption may then be continued so that the remaining volume of gas contained in the core can be measured and to permit the estimation of the long term diffusion coefficient. It is generally undesirable to grind the core to get a residual gas content as this destroys the core. Establishing a curve fit based on a long term diffusion coefficient enables the remaining gas to be estimated with good accuracy.

The retained core is kept for examination for cleats, permeability testing and shrinkage testing. Some may also be used for petrological determination.

Drill Stem Testing for Matrix Permeability, Reservoir Pressure, and Sorption Pressure

The next preferred operation is to undertake a DST test using a piece of equipment specifically developed for coal seam methane operations. The tool's operation is shown in Figures 1 to 8. This tool's operation may be summarized as follows:

1) Core is broken off and the inner barrel is retrieved.

2) The rods are withdrawn above the seam to be tested.

3) The DST tool is pumped down inside the rods to seat on the landing ring. In this state one packer extends through the core bit whilst the other remains inside the core barrel. As the drill string does not need to be pulled or another string run with the tool a significant time saving is achieved over other DST tools.

4) Pump pressure is raised to inflate the packers. This mode of operation makes the tool independent of electrical cables or and inflation line, considerable simplification. It also permits its use at significant depth.

Two options now exist, either to inject fluid into the seam or alternatively to produce from the seam.

In the case of injection:

5a) The drill string is rotated a ¼ turn to open the bottom valve.

6a) Water is injected at a constant pressure whilst flow is monitored. Several pressure steps are used.

In the case of production:

5b) The string is lowered to open the dump valve.

6b) Compressed air is applied to the top of the drill string to displace drilling fluid out of the dump valve.

7) The string is raised to close the dump valve and compressed air pressure is released.

8) A gas flowmeter is connected to the top of the string.

9) The string is rotated to open the bottom valve.

10) Fluid flow takes place from the seam and into the drill string. Gas flow is monitored by the gas flow meter whilst liquid is monitored by pressure build up in the string.

During the entire process pressures are automatically monitored in the bottom hole zone, in the annulus, in the string and in the packers.

11) The string is rotated to close the bottom valve.

12) A pressure build up takes place.

13) The string is rotated to open the bottom valve.

14) Pressures are permitted to equalize.

15) A wireline overshot is lowered into the string and latches onto the spearhead. It is pulled and opens a valve which deflates the packers.

16) The entire assembly is hoisted out of the drill rods on the wireline.

17) The chronological record of bottom hole pressure, annular pressure, packer pressure and pressure within the drill string is retrieved electronically from the assembly for analysis.

The injection test is useful in a water saturated seam because it permits the single phase permeability to be established. The step varied injection pressures also permit an apparent skin factor to be determined at various pressures. In our experience the skin factor in coal is pressure dependent and can be viewed as being associated with varying effective stress around the wellbore. Indeed by making assumptions about the pressure distribution and shape of the sorption pressure effective stress relationship (linear plot of log k vs effective stress) it is possible to derive a permeability pressure relationship from injection testing a well.

A production test is useful because it permits production of seam fluids and can permit the assessment of sorption
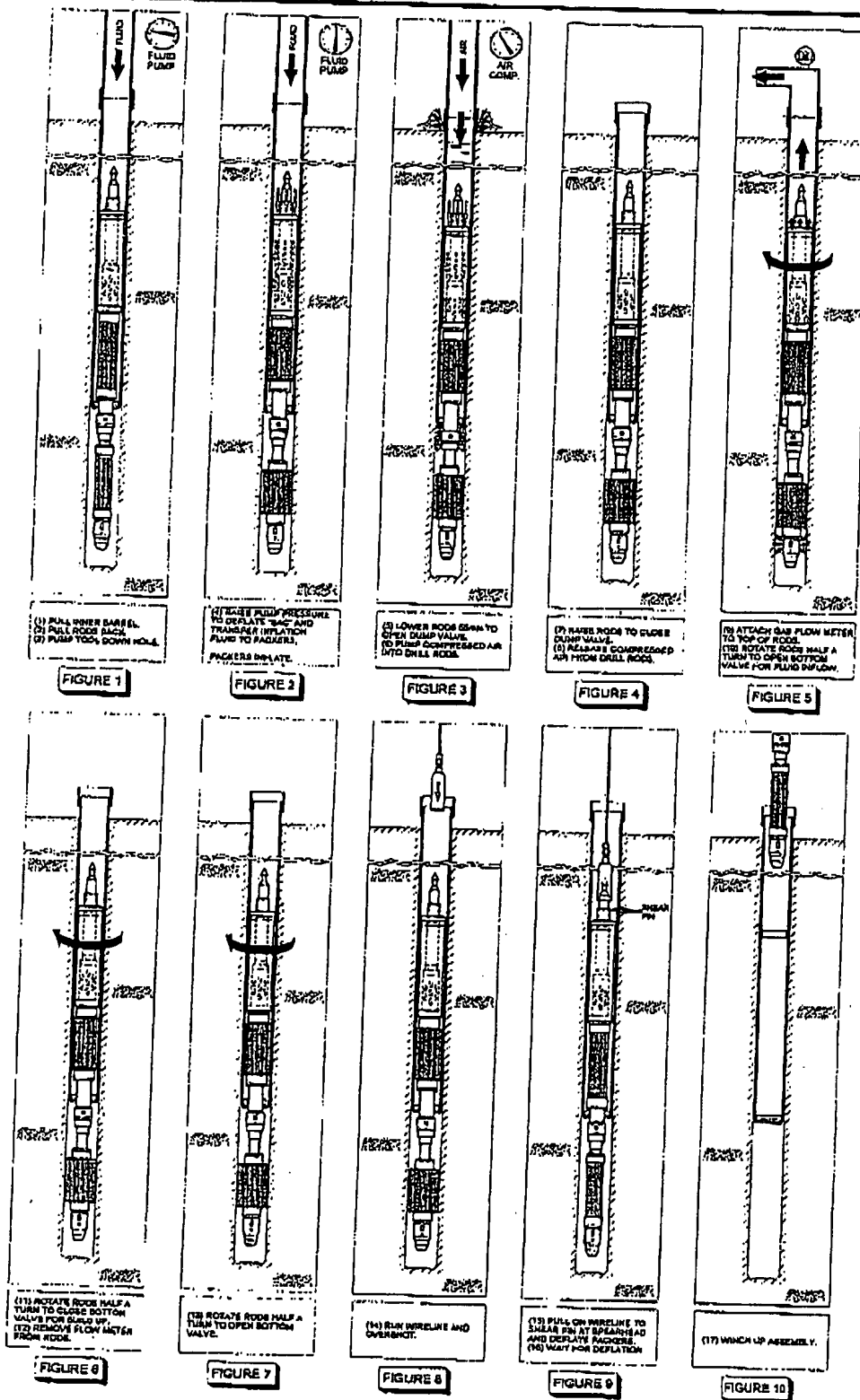
Bowen Basin Symposium 2000

pressure and reservoir pressure. In the event that gas is produced then the analysis for permeability is complicated by desorption effects and re-absorption of gas into the coal during the pressure build up phase. The process is one of gas being produced from the coal near the wellbore during the production phase. At the same time water and gas are produced along the cleats. When the well is closed pressures rise and the gas is re-absorbed back into the coal. When re-absorbtion is complete the area around the wellbore re-saturates and this is associated with a kick in the pressure response with time. This kick corresponds with the sorption pressure existing at that time.

Cleat Spacing

This can be assessed by visual examination of core or by optical/acoustic examination of the wellbore. In the event that cleats are not visible in sufficient number to determine their spacing and orientation then their effect on reservoir performance can only be assessed by a history matching of production and pressure with a simulator. This approach is fraught with problems of lack of uniqueness of solution.

Native Sorption Isotherms

The sorption pressure derived from the DST test and the sorption pressure gained by sealing the core in a water filled canister on surface when combined with a knowledge of gas contents at these two stages provides enough data to permit the form of a native sorption isotherm to be derived. It is still useful to undertake a laboratory isotherm test for comparison but preference should always be given to the native sorption isotherm especially in the case of mixed gases.

Fracture Permeability Assessment by Interference Tests

Once the DST test is complete it is usual practice to place packers fitted with pressure transducers over the seams in boreholes affected by subsequent testing or production. An alternative is to grout pressure transducers in place but this can lead to problems with channelling in the grout if the reservoir pressures are greater than hydrostatic. The placement of such pressure transducers is essential for establishing fracture permeability and is invaluable for reservoir monitoring during subsequent extraction.

The placement of pressure transducers in monitoring holes around an injection or production hole enables the testing to take place for fracture permeability. In a saturated system injection yields the best results because flow remains in a single phase and the permeability results are easy to analyse. If free gas exists in the reservoir it is a better option to produce from the well. Such an interference test can be made part of a production operation.

Shrinkage/Stress Effects

The assessment of the effects of shrinkage and effective stress on permeability can be made by two laboratory/field techniques or by a production test. The latter takes a long time while the field/laboratory tests can be undertaken relatively quickly. Two effects need to be known. The first is the effective stress/permeability relation and the second is the gas content shrinkage behaviour. In addition a knowledge of the stress field is required.

The effective/stress permeability relation can either be obtained through careful analysis of the change in skin effect brought about by varying injection pressures to a well or by laboratory testing. Both are useful and may yield similar or varying results. The laboratory testing involves placing the vertical core in a triaxial test rig and passing gas transversely across the core. The total vertical stress is maintained whilst the lateral confining stress is varied. The use of helium or nitrogen as the gas restricts the effects of shrinkage/growth of the coal thus enabling the derivation of a straightforward effective lateral stress/permeability relation.

Coal expansion and shrinkage is best assessed by strain gauging core and by placing it in a vessel which can be filled with gas at a series of controlled pressures. Between changes in pressure the core is allowed to approach equilibrium and the strain changes are recorded. Equilibrium is never reached however and numerical assumptions on the nature of absorbtion need to be made to arrive at the final strain/gas pressure relationships. The original design of the core permeability test rig was to permit strain gauged core to be used in the cell and to fully gas the core and then to bring it up to *in situ* stress levels. The intention was then to hold a constant lateral strain whilst reducing gas pressure and permitting flow through the core, thus providing a measurement of changes in permeability with varying gas pressure and levels of sorption. This has never been able to be realized however because of the long duration required for the tests. To undertake such testing the rig could be easily tied up for 3–6 months on a single piece of core. It was nearly impossible to keep strain gauges operational under conditions of stress, gas and moisture for this period of time. In addition it was grossly inefficient to tie up the permeability rig for this period hence the use of the separated effective stress/permeability and shrinkage/sorption tests. The alternative of permeability testing at varying effective stresses combined with separate sorption/shrinkage testing has proven faster and more cost efficient.

It is worth noting that not all coals show significant changes in effective stress with permeability. Some of the harder coals show negligible change.

Domains

Some coal seam methane reservoirs are noted as having significant spatial changes in behaviour. These can commonly be related to changed stress situations or to the history of groundwater movement. Geological studies may

Bowen Basin Symposium 2000

320

Seam Gas

reveal potential zonal differences. Often however these changes are found as the result of drilling and testing. Only when the tests have been performed can the geology be re-examined and conclusions drawn about which domains of varying reservoir behaviour may exist.

to production testing. Emphasis has been placed on measuring relevant parameters rather than attempting to history match production data utilizing a reservoir simulator. The latter approach suffers from a lack of uniqueness of solution that may lead to significant errors in estimation of long term reservoir performance.

CONCLUSIONS

This paper presents the techniques required to establish the behaviour of coal seam methane reservoirs without recourse

The test techniques described yield results on reservoir behaviour more quickly and cheaply than production testing.

Ian Gray,
Principal, Sigra Pty Ltd., 72 Donaldson Rd, Rocklea, Brisbane, Qld, 4106

Bowen Basin Symposium 2000

M&H   McCormick, Paulding & Huber LLP
Intellectual Property Law

Offices in
Hartford, CT and
Springfield, MA

From the desk of
Gerald L. DePardo
depardo@ip-lawyers.com
Tel 860. 549.5290
Fax 860. 527.0464

CityPlace II
185 Asylum Street
Hartford, CT
06103-3410
www.ip-lawyers.com

John C. Linderman*✦
J. Kevin Grogan*✦
Marina F. Cunningham*
Daniel G. Mackas*
Nicholas J. Tuccillo*
Wm. Tucker Griffith*
Gerald L. DePardo*
Donald J. MacDonald✦
Kevin H. Vanderleeden✦
Jeanne M. Tanner*
John A. Kramer✦
Emily J. Kasperowski✦
Chad M. Rink*✦
Justin R. Sauer*
Edgar G. Rodriguez*
*Admitted in CT
✦Admitted in MA

Technical Assistant
Alexander E. Andrews

Of Counsel
Arthur F. Dionne*✦
Donald K. Huber*
John C. Hilton*
Frederick J. Haesche*
Chester E. Flavin✦
William C. Crutcher*

May 3, 2007

<u>Sent Via Federal Express</u>

Luke Santangelo, Esq. (USPTO Reg. No. 31,997)
Santangelo Law Offices, P.C.
125 South Howes Street, Third Floor
Fort Collins, CO 80521

Re: Information Material to Patentability of pending patent applications:
    1) Serial No. 10/789,974, entitled "Methods of Evaluating Understaturated Coalbed
    Methane Reservoirs", to Carlson, filed February 28, 2004; and
    2) Serial No. 11/412,674, entitled "Methods of Quantifying Gas Content of a Gas-Sorbed
    Formation Solid", to Carlson, filed April 26, 2006 (which is a continuation of above case,
    Serial No. 10/789,974).

Dear Attorney Santangelo,

    This letter is regarding the subject patent applications, of which you are an attorney of record, and is sent on behalf of our client, Welldog, Inc. and Welldog Holdings. A copy of this letter with enclosures has also been sent to Yates Petroleum Corporation, assignee of the subject patent applications.

    Enclosed are copies of the following three prior art references we believe are relevant and material to the patentability of the subject patent applications:

    1) Z. Weishauptova and J. Medek, "Bound forms of methane in the porous system of coal", Fuel 1998, Vol. 77, No. 1/2, pp 71-76;
    2) J. J. Kipling, "Adsorption from Solutions of Non-Electrolytes", Academic Press 1965, pp 86-89; and
    3) I. Gray, "Determining Gas Production Characteristics of Coal Seams", Bowen Basin Symposium 2000, pp 315-320.

    In particular, the first reference, by Z. Weishauptova, et al., describes the relationship between the gas content in water and the partial pressure (P) of methane (i.e., methane's "bubble point" pressure in the water) using the well-known Henry's Law (Eq. 6, pg 72 and related text). This reference also describes the relationship between the gas content of the coal and the partial pressure (P) of methane (i.e., the "critical desorption pressure" or CDP of the coal), using the well-known Langmuir isotherm (Eq. 8, pg 74 and related text). Accordingly, this reference teaches that the equivalent partial pressure of methane in the water (or methane's "bubble point" pressure in the water) is equivalent to the CDP of the coal, by use of the same partial pressure (P) of methane in both Equations 4 and 8. Moreover, this reference teaches that the methane content in the coalbed can be calculated from the gas content in the water using the partial pressure (P) of methane.

Luke Santangelo, Esq.
May 3, 2007
Page 2

The second reference, by J. J. Kipling, describes a method of calculating the concentration of dissolved gas (or gas content) in solution (e.g., water) from the pressure in the gas phase (or equivalent "gas pressure" or partial pressure of gas in the solution), using well-known Bunsen coefficients, similar to Henry's Law, and the inverse method of calculating an equivalent "gas pressure" from the dissolved gas concentration of the solution (pg 86, second parag. and Fig. 6.1(b)). In addition, this reference teaches that this same equivalent "gas pressure" can be plotted on an adsorption isotherm (e.g., the well known Freundlich isotherm), to determine the quantity of gas adsorbed by (or gas content of) the charcoal solid (pg 86, second parag. and Fig. 6.1(a)). Further, the reference states: "In general, it may be expected that adsorption of most gases from solution will follow this pattern" (pg 86, third parag.). Accordingly, this reference teaches that the equivalent partial pressure of a gas (e.g., ethylene) in water (or the gas' "bubble point" pressure in the water) is equivalent to the partial gas pressure of an adjacent solid used with adsorption isotherms (i.e., the critical desorption pressure or CDP of the solid), by use of the same partial pressure of the gas in both Figs. 6.1(a) and 6.1(b). In addition, this reference teaches that the gas content in a solid (e.g., charcoal) can be calculated from the gas content in the adjacent liquid (e.g., water) using the partial pressure of the gas. Further, this reference teaches that the above general principles apply for most gases adsorbed from solution.

The third reference, by I. Gray, states "The gas is stored in the coal at sorption pressure which is the equivalent of the bubble point in a conventional reservoir." (pg 315, fourth parag.). Accordingly, Gray teaches that the bubble point of the water in a reservoir is equivalent to the sorption pressure (or "critical desorption pressure" or CDP) of the coal.

Therefore, as many of the pending claims of the subject patent applications are based on the principles taught by the enclosed references, the enclosed references are highly relevant and material to the patentability of the pending claims of the subject patent applications. In particular, the enclosed references teach information that is claimed in the subject patent applications and is described therein as significant to the invention (see at least paragraph numbers 18, 20, and 51 of both subject patent applications, paragraph 59 of the '974 application and corresponding paragraph 58 of the '674 application). For example, without limitation, paragraph 18 states, "In addition, the invention shows that the test of the water can even permit inductive quantification of the critical desorption pressure of the coal in an undersaturated coalbed methane reservoir."; paragraph 20 states, "The present invention teaches that the bubble point of the formation water can be used to inductively quantify the CDP of the coal in the coalbed methane reservoir..."; paragraph 51 states, "In fact the present invention has discovered that the value of the bubble point pressure of the formation water can be equated to the CDP of the coal."; and paragraphs 59/58 states, "A significant aspect of the present invention is its realization that the bubble point pressure of an entirely different substance, namely the formation water, can be used to inductively quantify the critical desorption pressure of the coal." After reviewing the enclosed references, you may find additional information therein that is material to the patentability of the subject patent applications.

As you are aware, each individual associated with the filing and prosecution of a patent application has a duty of candor and good faith in dealing with the United States Patent and Trademark Office (USPTO), which includes a duty to disclose to the USPTO all information known to that individual to be material to patentability, pursuant to 37 CFR 1.56 "Duty of Disclosure, Candor and Good Faith." Otherwise, any patents issuing therefrom will be held unenforceable as a result of knowingly withholding such material information from the USPTO.
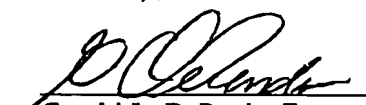
Luke Santangelo, Esq.
May 3, 2007
Page 3

As you are also aware, after payment of the issue fee, the applicant may request that information material to patentability be considered by the USPTO by filing a Request for Continuing Examination and a Petition pursuant to 37 CFR 1.313(c) "Withdrawal from Issue". Alternatively, other steps may be taken to withdraw a patent application from issue, as described in 37 CFR 1.313(c).

In the event that you choose not to withdraw the subject patent applications from issue and they become granted US Patents, we will promptly file a declaratory judgment action to have the patents declared invalid and unenforceable in view of the enclosed prior art references. We will also seek a preliminary injunction to prevent the patentee from contacting any of our client's customers with regard to the invalid and unenforceable patents, in view of your prior threatening correspondence to our client, dated March 22, 2006, a copy of which is enclosed herewith.

After you have reviewed the enclosed references, if you should have any questions, please feel free to contact me.

Sincerely,

Gerald L. DePardo, Esq.

/Enclosures:
1) Z. Weishauptova and J. Medek, "Bound forms of methane in the porous system of coal", Fuel 1998, Vol. 77, No. 1/2, pp 71-76.
2) J. J. Kipling, "Adsorption from Solutions of Non-Electrolytes", Academic Press 1965, pp 86-89.
3) I. Gray, "Determining Gas Production Characteristics of Coal Seams", Bowen Basin Symposium 2000, pp 315-320.
4) Letter from Luke Santangelo to Wayne Greenberg, dated March 22, 2006.

Copy (with enclosures) to:

David Lanning
Assistant Vice President
Yates Petroleum Corporation
105 South Fourth Street
Artesia, New Mexico 88210-2118

Luke Santangelo
    Patent & Trademark Attorney
Cheryl L. Anderson
    Trademark Attorney
Al Wiedmann Jr.
    Patent Attorney
Kay L. Collins
    Trademark Attorney
Nicole A. Ressue
    Patent Attorney
Misha Gregory Macaw
    Patent Attorney

SANTANGELO LAW OFFICES, P.C.

125 South Howes Street
Third Floor
Fort Collins, CO 80521
United States of America

Telephone: (970) 224-3100
Facsimile: (970) 224-3175
ideas@IdeaAssetGroup.com

May 14, 2007

Gerald L. DePardo, Esq.   Sent Via Federal Express
McCormick, Paulding & Huber LLP
City Place II
185 Asylum Street
Hartford, CT 06103-3410

      Re: Reference Materials

Dear Mr. DePardo,

      Thank you very much for your letter. We appreciate the new references that you have provided to us; we were not previously aware of them. You should know that we certainly only desire valid enforceable patents as we are not trying to hide anything. Therefore, to make sure the government has all the information and to satisfy our Rule 56 duty under U.S. patent law, we have filed petition documents submitting the references. As we await a response from the patent office, we can represent to you that we will not take immediate action and will also provide you the courtesy of letting you know how the patent office responds.

      It is curious to us that these references are now being sent to us only days before issuance of the first patent. Would you please tell us when Welldog or your firm first discovered them? Since we first visited with Welldog on May 3, 2005 about licensing, we understood the concern that Yates Petroleum's patents would obsolete much of Welldog's business. We are curious if your arguments and the 11th hour disclosure are somehow being used as a business tactic to try to avoid issuance while Welldog adapts its business to the realities of our new technology.

      You should also know, however, that we disagree with your conclusions. In fact, your arguments seem largely based upon the Gray reference. We have previously cited other materials by Mr. Gray to the patent office, namely, a patent and an article. The Gray disclosures were even discussed in Yates Petroluem's patent applications. Those in the art had not appreciated the extension of technology that the Yates' applications disclose. This confirmed the candid concern that our new technology might cut the legs out from years of investment, and spontaneously upon technical disclosure of our new technology that the patent application's observations suggesting that everyone had felt you had to be in contact with the coal to get the desired information was indeed correct.

The Idea Asset Group

The Weishauptova article deals with methane at temperatures above the critical temperature and which is saturated; therefore, this article is not relevant to the Yates Petroleum's patent applications at in least that their claims are specific to undersaturated reservoirs. Of note, the terms "critical desorption pressure" and/or "bubble point" are not mentioned in the Weishauptova reference and, furthermore, a bubble point may not even be relevant in a saturated system such as described in this article. In addition, we believe the Kipling reference is not related to, does not teach, and does not even make obvious the Yates Petroleum's claimed invention(s). This reference does not discuss the gas content of methane reservoirs or coalbed methane reservoirs or the like. Thus, your materials seem largely duplicative of what the examiner at the United States Patent and Trademark Office already considered in examining – and allowing – the patent applications. In other words, we still believe that the government examiner got it right in allowing the cases. The Yates Petroleum's patents are valid. While we appreciate your advocacy role to try to negate a serious impact on Welldog's business, we believe your rationales are unfounded.

Understand that we appreciate how Yates Petroleum's technology could cut the legs out from Welldog. While we still believe that Welldog will need rights to compete in the marketplace, we have not yet undertaken an analysis of infringement relative to Welldog's current technology. Indeed, so long as Welldog uses only what we are aware of as its present technology and is not doing development in our area, an assessment of patent coverage might not become necessary for purely economic reasons to consumers. If, or once, we conduct an analysis of Welldog's current technology, and if, or once, an intent to pursue an action against Welldog becomes ripe, we intend to engage in discussion with you to make sure issues have either been resolved or at least have reached an impasse to an end result.

We are, of course, mindful of your declaratory judgment threat. While we recognize that this threat makes it necessary to preserve various rights until your concerns have been more formally addressed, we do not intend to immediately assert an infringement action against Welldog or its customers. Indeed, we will even go so far as to act against our own interests and will not serve you with an action until we have had some chance to discuss it with you.

Again, our goal is to obtain valid and enforceable patents, and to this end we believe that dialogue would be advisable. We will certainly engage in that dialogue to try to address the issues short of legal action if possible.

Sincerely,
SANTANGELO LAW OFFICES, P.C.

Luke Santangelo